



## Reducing diffusion-induced stresses of electrode–collector bilayer in lithium-ion battery by pre-strain

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### HIGHLIGHTS

- We report a novel strategy of pre-strain applied to the electrode–collector bilayer.
- Pre-strain greatly alleviates built-in stresses due to lithium-ion diffusion.
- Owing to pre-strain, stress drop at the electrode–collector interface is suppressed.
- Tensile stresses of electrode surfaces should be tailored by tuning pre-strain.

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### ABSTRACT

Diffusion-induced stresses can break structure integrity of electrodes, and further degrade storage capacity and cycling stability of lithium-ion batteries. To reduce these built-in stresses due to lithium-ion diffusion, we report a strategy of pre-strain applied to the structure of active electrode film bonded to the current collector. Accordingly, a model is developed for the effect of pre-strain on mechanical stress of the electrode–collector structure. The theoretical results show that pre-strain greatly alleviates diffusion-induced stresses of electrode film and current collector, especially stress drop at the electrode–collector interface. In addition, tensile stresses of two electrode surfaces should be modestly tuned by pre-strain, avoiding brittle fracture.

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## 1. Introduction

Lithium-ion batteries, as energy storage elements, are widely used in portable electronic devices and have the promising applications in electric vehicles. Owing to the rise of novel electrode materials with large storage capacity and high power density, lithium-ion batteries have attracted increasing research interests recently. These novel materials, such as nanostructure-based battery electrodes [1–5] and core–shell electrodes [6–9], exhibit high reversible charge capacity and cycling stability during lithium reactions due to their relatively short transport pathways, high active surfaces, and excellent tolerance to mechanical stress.

Electrode materials experience significant volume changes involved in the electrochemical reactions, leading to electrode

pulverization and the resultant loss of electrical contact from the current collector. As a result, electrode fracture has been recognized as one of the origins in the capacity degradation of battery [10,11], and diffusion-induced stresses are extensively studied in the existing literature [12–17]. Huggins and Nix presented a simple one-dimensional model of decrepitation, which predicted the terminal electrode particle size using the Griffith criterion [18]. Christensen and Newman developed a coupled diffusion-stress model for estimating stress generation in  $\text{Li}_y\text{Mn}_2\text{O}_4$  ( $0 < y < 2$ ) due to lithium intercalation [19]. A cohesive model of crack nucleation in an initially crack-free strip electrode was developed by Bhandarkar and Gao [20], which identified a critical characteristic dimension below which crack nucleation became impossible. Recently, Zhao [21] and Cui [22] investigated silicon electrodes with large elastic–plastic deformation in high-capacity lithium-ion batteries. In these previous studies, most of the models focused on diffusion-induced stresses and fracture of single electrode particle and neglected the influence of the current collector. Until recently, Zhang et al. comprehensively discussed the

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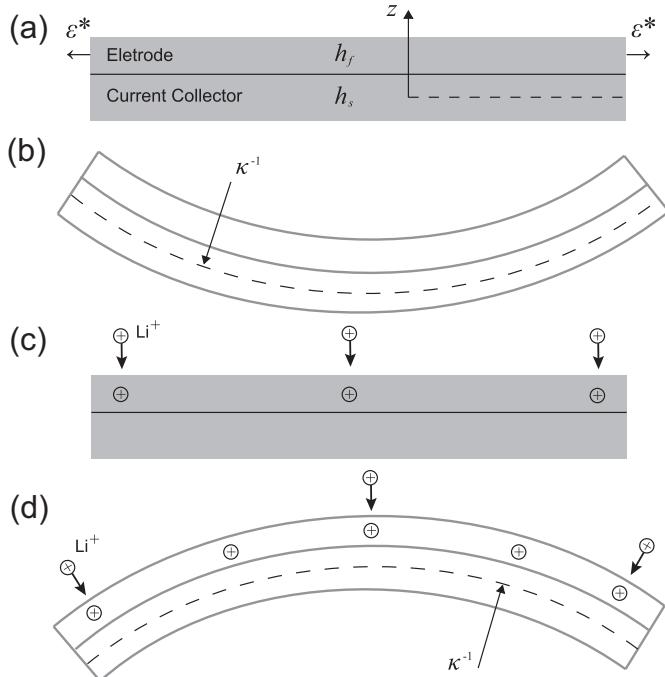
layered structural configuration including active electrode film and the current collector, aiding the design and optimization of lithium-ion battery from the viewpoint of mechanics [23,24].

In the present work, we report an effective strategy of pre-strain applied to the electrode–collector bilayer to reduce diffusion-induced stresses and resist fracture, and accordingly develop a model for the effect of pre-strain on mechanical stress inside the bilayer structure. As shown in Fig. 1, the electrochemical-active electrode film is bonded to a current collector that forms an electric transport path. The electrode film experiences a biaxial stretching before lithium-ion insertion, where the biaxial tension is maintained by externally applied tension and the current collector is unrestrained. Once the externally applied traction is relaxed, the pre-strain in the electrode induces a curvature in the electrode–collector structure. Then, as lithium-ions gradually insert into the electrode, the curvature vanishes and reverses shown in Fig. 1c and d, respectively.

## 2. Basic theory

### 2.1. Biaxial stresses of the electrode–collector structure

As depicted in Fig. 1, the mid-plane of the current collector is positioned in  $xy$ -plane with the thickness of  $h_s$  along  $z$ -direction, and the collector is perfectly bonded to the active electrode film with the thickness of  $h_f$ . On account of the asymmetry of configuration, the electrode–collector bilayer should bend due to the pre-strain. In addition, we assume that the stress components along  $z$ -axis are neglected because of the free surface and a very small extent in the thickness direction compared to the in-plane dimensions. According to mechanical equilibrium and the deformation compatibility [23], the in-plane biaxial strain varies linearly with respect to the vertical coordinate  $z$ , which can be expressed as



**Fig. 1.** (a) Sketch of pre-strained electrode film bonded to the current collector, where the pre-strain is maintained by externally applied tension and the current collector is unrestrained. (b) If the externally applied traction is relaxed, the mismatch strain in the electrode induces a curvature in the electrode–collector structure. As lithium-ions insert into the electrode, the curvature vanishes and reverses corresponding to (c) and (d), respectively.

$$\varepsilon = \varepsilon_0 - \kappa z. \quad (1)$$

where  $\varepsilon_0$  is the extensional strain of the collector mid-plane,  $\kappa$  represents the curvature of the deformed bilayer. The active electrode film carries a mismatch elastic strain in the form of an isotropic equibiaxial extensional strain parallel to the interface, including the pre-strain and diffusion-induced strain, which takes the following form

$$\varepsilon_t(z, t) = \begin{cases} 0 & \text{for } -\frac{1}{2}h_s \leq z \leq \frac{1}{2}h_s, \\ \varepsilon^* - \frac{1}{3}\Omega c(z, t) & \text{for } \frac{1}{2}h_s \leq z \leq \frac{1}{2}h_s + h_f. \end{cases} \quad (2)$$

where  $c$  is the molar concentration of lithium-ion, and  $\Omega$  is the partial molar volume of solute.

Because the state of the key deformation is equi-biaxial strain at each point, the resistance to the deformation can be represented in terms of the biaxial elastic modulus  $M$ , namely

$$M = \frac{E}{1-\nu}. \quad (3)$$

$E$  is the Young's modulus and  $\nu$  is Poisson's ratio, implying that isotropic elasticity analysis of infinitesimal deformation is performed. The biaxial modulus throughout the electrode–collector structure is denoted by

$$M(z) = \begin{cases} M_s & \text{for } -\frac{1}{2}h_s \leq z \leq \frac{1}{2}h_s, \\ M_f & \text{for } \frac{1}{2}h_s \leq z \leq \frac{1}{2}h_s + h_f. \end{cases} \quad (4)$$

Here,  $M_s$  is the biaxial modulus of the current collector, and  $M_f$  for the electrode film.

We treat the mechanical equilibrium as a static equilibrium problem due to the much faster velocity of elastic deformation over lithium-ion diffusion in electrode material. Following Prussin's previous work [25], we introduce diffusion-induced stresses by analogy to thermal stress. Thereby, the stress–strain relations, taking into account the mismatch strain in electrode film, can be written as [26]

$$\sigma(z, t) = M(z)[\varepsilon_0 - z\kappa + \varepsilon_t(z, t)], \quad -\frac{1}{2}h_s \leq z \leq \frac{1}{2}h_s + h_f. \quad (5)$$

Further, the strain energy density throughout the system is then

$$U(z, t) = M(z)[\varepsilon_0 - z\kappa + \varepsilon_t(z, t)]^2. \quad (6)$$

Integrating the above equation with respect to  $z$  yields the total strain energy as

$$V(\varepsilon_0, \kappa) = \int_{-h_s/2}^{h_s/2+h_f} U(z, t) dz = \varepsilon_0^2 C_{0,0} - 2\varepsilon_0 \kappa C_{1,0} + \kappa^2 C_{2,0} - 2\kappa C_{1,1} + C_{0,2} + 2\varepsilon_0 C_{0,1}. \quad (7)$$

where

$$C_{m,n} = \int_{-h_s/2}^{h_s/2+h_f} z^m M(z) \varepsilon_t(z, t)^n dz. \quad (8)$$

For any particular system, the quantity  $C_{m,n}$  is constant for any choice of integer values for  $m$  and  $n$ .

Within the class of permissible deformations, the actual mid-plane deformation renders the total potential energy  $V(\varepsilon_0, \kappa)$  stationary with respect to variations in  $\varepsilon_0$  and  $\kappa$ , which requires  $\partial V/\partial \varepsilon_0 = 0$  and  $\partial V/\partial \kappa = 0$ , respectively, thereby leading to

$$\varepsilon_0 = \frac{C_{1,1}C_{1,0} - C_{0,1}C_{2,0}}{C_{2,0}C_{0,0} - C_{1,0}^2}, \quad \kappa = \frac{C_{1,1}C_{0,0} - C_{0,1}C_{1,0}}{C_{2,0}C_{0,0} - C_{1,0}^2}. \quad (9)$$

It is obvious that  $\varepsilon_0$  and  $\kappa$  are time dependent through  $C_{0,1}$  and  $C_{1,1}$ , while other  $C_{m,n}$  contribute to a time independent impact. To ultimately obtain the biaxial stress in Eq. (5), the lithium-ion distribution must be figured out, which should be discussed in the next section.

## 2.2. Diffusion equation and dimensionless results

For simplicity, we neglect stress effect on the diffusion process due to hydrostatic stress gradient (see Appendix), since this effect only gives quantitative modifications without changing the conclusions and trends reported here. Furthermore, it is assumed that two or more phase transitions do not occur in the inner electrode materials during lithium insertion/extraction [15,19]. As a result, we can obtain the diffusion equation describing the solute concentration distribution with varying time

$$\frac{\partial c}{\partial t} - D \frac{\partial^2 c}{\partial z^2} = 0. \quad (10)$$

where  $D$  is diffusion coefficient. In this study, we assume that the electrode is initially at a uniform concentration, and the lithium-ion flux keeps uniform  $J_0$  over the upper surface, namely galvanostatic operation [27]. And the initial and boundary conditions take the forms

$$\begin{aligned} c(z, t=0) &= c_0, \\ D \frac{\partial}{\partial z} c \left( z = \frac{1}{2}h_s, t \right) &= 0, \\ D \frac{\partial}{\partial z} c \left( z = \frac{1}{2}h_s + h_f, t \right) &= J_0. \end{aligned} \quad (11)$$

$c_0$  is an initial concentration distribution inside the electrode film, and the aforementioned expressions can be applied to the lithium-ion diffusion during charging and discharging;  $c_0 = 0$  and  $J_0 = J_s$  are set for the process of lithium insertion; while  $c_0 = c_{\max}$  and  $J_0 = -J_s$  for lithium extraction, where  $c_{\max}$  is the maximum lithium-ion concentration existing in the electrode.

Similar to the solution of the temperature distribution given by Carslaw and Jeagar [28], the analytic solution of this diffusion problem is reproduced here

$$\begin{aligned} c(z, t) - c_0 &= \frac{J_0 h_f}{D} \left\{ \frac{Dt}{h_f^2} + \frac{1}{2h_f^2} \left( z - \frac{h_s}{2} \right)^2 - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \right. \\ &\quad \times \exp \left( - \frac{n^2 \pi^2 D t}{h_f^2} \right) \cos \left[ \frac{n\pi}{h_f} \left( z - \frac{h_s}{2} \right) \right] \left. \right\}. \end{aligned} \quad (12)$$

In order to extract intrinsic results, we introduce the following dimensionless lithium-ion concentration and biaxial stress

$$\bar{c} = \frac{c}{c_{\max}}, \quad \bar{c}_0 = \frac{c_0}{c_{\max}}, \quad \bar{\sigma} = \frac{\sigma}{\frac{1}{3}Q c_{\max} M}. \quad (13)$$

Likewise, the corresponding dimensionless variables are also defined as

$$\bar{z} = \frac{z}{h_f}, \quad \bar{h} = \frac{h_s}{h_f}, \quad \bar{M} = \frac{M_s}{M_f}, \quad \bar{\varepsilon}^* = \frac{\varepsilon^*}{\frac{1}{3}Q c_{\max}}, \quad \bar{t} = \frac{Dt}{h_f^2}, \quad \bar{I} = \frac{J_0 h_f}{D c_{\max}}. \quad (14)$$

Here,  $\bar{t}$  is the dimensionless time, and  $\bar{I}$  is the dimensionless current density. It is noted that the product must satisfy that  $\bar{t} \leq 1$ , and the equal sign implies the case when the active electrode is fully lithiated. By using these dimensionless quantities, the concentration distribution can be transformed into the following form

$$\begin{aligned} \bar{c} - \bar{c}_0 &= \bar{I} \left\{ \bar{t} + \frac{1}{2} \left( \bar{z} - \frac{1}{2} \bar{h} \right)^2 - \frac{1}{6} - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \right. \\ &\quad \times \exp \left( - n^2 \pi^2 \bar{t} \right) \cos \left[ n\pi \left( \bar{z} - \frac{1}{2} \bar{h} \right) \right] \left. \right\}. \end{aligned} \quad (15)$$

Considering Eqs. (2), (5) and (9), we can rewrite the dimensionless biaxial stress in the electrode film as

$$\bar{\sigma} = \frac{\bar{C}_{1,1}\bar{C}_{1,0} - \bar{C}_{0,1}\bar{C}_{2,0}}{\bar{C}_{2,0}\bar{C}_{0,0} - \bar{C}_{1,0}^2} - \frac{\bar{C}_{1,1}\bar{C}_{0,0} - \bar{C}_{0,1}\bar{C}_{1,0}}{\bar{C}_{2,0}\bar{C}_{0,0} - \bar{C}_{1,0}^2} \bar{z} + (\bar{\varepsilon}^* - \bar{c}), \quad (16)$$

where

$$\begin{aligned} \bar{C}_{0,0} &= 1 + \bar{h}\bar{M}, \\ \bar{C}_{1,0} &= \frac{1}{2} (1 + \bar{h}), \\ \bar{C}_{2,0} &= \frac{1}{3} \left[ \left( 1 + \frac{1}{2} \bar{h} \right)^3 - \left( \frac{1}{2} \bar{h} \right)^3 \right] + \frac{1}{12} \bar{h}^3 \bar{M}, \\ \bar{C}_{0,1} &= \bar{\varepsilon}^* - (\bar{c}_0 + \bar{I} \bar{t}), \\ \bar{C}_{1,1} &= \frac{1}{2} \bar{\varepsilon}^* (1 + \bar{h}) - \left\{ \frac{1}{2} \bar{c}_0 (1 + \bar{h}) + \bar{I} \left[ \frac{1}{2} \bar{t} (1 + \bar{h}) + \frac{1}{24} \right. \right. \\ &\quad \left. \left. - \frac{2}{\pi^4} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^4} (\cos n\pi - 1) \exp(-n^2 \pi^2 \bar{t}) \right] \right\}. \end{aligned} \quad (17)$$

For the stress of the current collector, the last terms bracketed together in Eq. (16) should be removed, which reads

$$\bar{\sigma} = \frac{\bar{C}_{1,1}\bar{C}_{1,0} - \bar{C}_{0,1}\bar{C}_{2,0}}{\bar{C}_{2,0}\bar{C}_{0,0} - \bar{C}_{1,0}^2} - \frac{\bar{C}_{1,1}\bar{C}_{0,0} - \bar{C}_{0,1}\bar{C}_{1,0}}{\bar{C}_{2,0}\bar{C}_{0,0} - \bar{C}_{1,0}^2} \bar{z}. \quad (18)$$

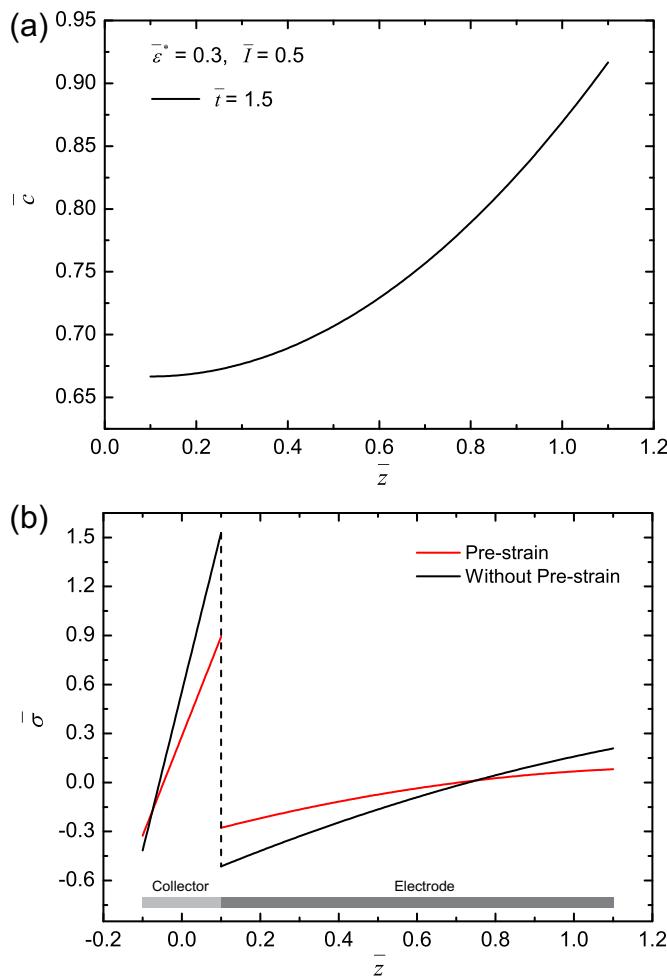
Compare Eq. (16) with (18), we can see that the distribution of stress in the current collector exhibit linearly variation through the thickness direction, while a more complicated stress field presents in the electrode film due to the term of lithium-ion concentration.

## 3. Results and discussion

To clearly probe the influence of pre-strain, we take a specific electrode–collector structure as an example. In our model, the thickness ratio of  $h_s/h_f = 0.2$  is assumed, which is a reasonable value based on the factors hereinafter. The collector should be thin enough to reduce weight without decreasing the electrode capacity, since the collector should not be involved in electrochemical reactions. On the other hand, the collector should possess a sufficient thickness, otherwise the collector experiences an excessive tensile stress located at the electrode–collector interface, which can be identified in the following study. With respect to  $M_s/M_f$ , we fix it at 10. Metal collector is widely employed in lithium-ion

battery, such as copper. However, the conventional electrodes include carbon, LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, LiFePO<sub>4</sub>, etc. The biaxial elastic modulus of the former is almost an order higher than that of the latter, as a result,  $M_s/M_f = 10$  is applicable. We state that this work merely estimates the effect of pre-strain on diffusion-induced stresses, and the influences of the thickness ratio  $h_s/h_f$  and the modulus ratio  $M_s/M_f$  have been discussed in a previous paper by Zhang [23].

First, we compare two cases: one including the pre-strain and the other without the pre-strain, aiming at revealing the effect of pre-strain. Fig. 2 illustrates the dimensionless concentration and biaxial stress at the dimensionless time  $\bar{t} = 1.5$  during lithium-ion insertion, where the dimensionless pre-strain and current density are  $\bar{\varepsilon}^* = 0.3$  and  $\bar{I} = 0.5$ , respectively. For the simplified diffusion equation in Eq. (10), the diffusion process is decoupled from mechanical deformation, and the pre-strain does not affect lithium-ion concentration distribution. Lithium-ions first diffuse into the electrode film through the upper surface, and gradually transfer inside due to the concentration gradient. Therefore, as shown in Fig. 2(a), the concentration becomes low with decreasing  $\bar{z}$ . In fact, the concentration gradient strongly depends on the current density, that is, the larger current density, the larger concentration gradients, which subsequently leads to the larger diffusion-induced stresses.



**Fig. 2.** The results for electrode–collector bilayer film at the dimensionless time  $\bar{t} = 1.5$  during lithium-ion insertion: (a) lithium-ion concentration and (b) biaxial stress.

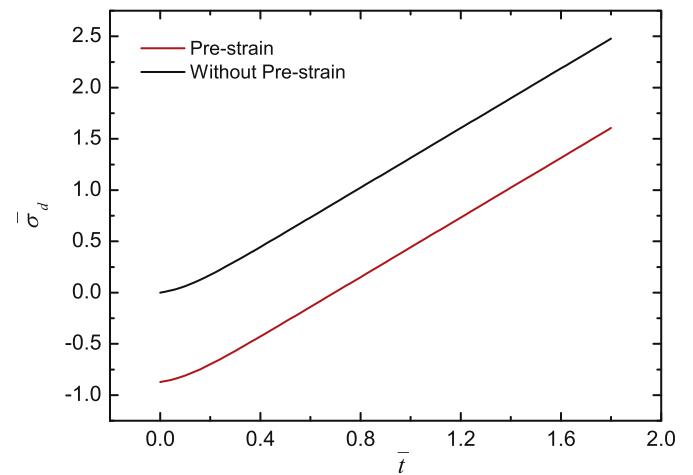
Fig. 2(b) shows the corresponding biaxial stress when the dimensionless time  $\bar{t} = 1.5$ . Compared to the case without pre-strain, the biaxial stresses both in the collector and electrode film are greatly alleviated by applying the pre-strain. This inspiring result could be easily understood. At the beginning, the electrode film experiences a tensile pre-strain, inducing a curvature in the electrode–collector structure as depicted in Fig. 1(b). As lithium-ions insert into the electrode, the curvature gradually reduces and reverses shown in Fig. 1c and d, respectively. In other words, the initial stresses resulting from the pre-strain are compensated by partly inverse diffusion-induced stresses, thereby reducing total built-in stresses within the electrode–collector structure. In addition, the maximum tensile stress of the current collector occurs at the electrode–collector interface, and the maximum compressive stress of the electrode film also arises there, resulting in a large stress drop at the interface. Here, according to Eqs. (16) and (18), we can draw this stress drop as

$$\bar{\sigma}_d = \bar{\sigma}_s - \bar{\sigma}_f = \bar{c} - \bar{\varepsilon}^*. \quad (19)$$

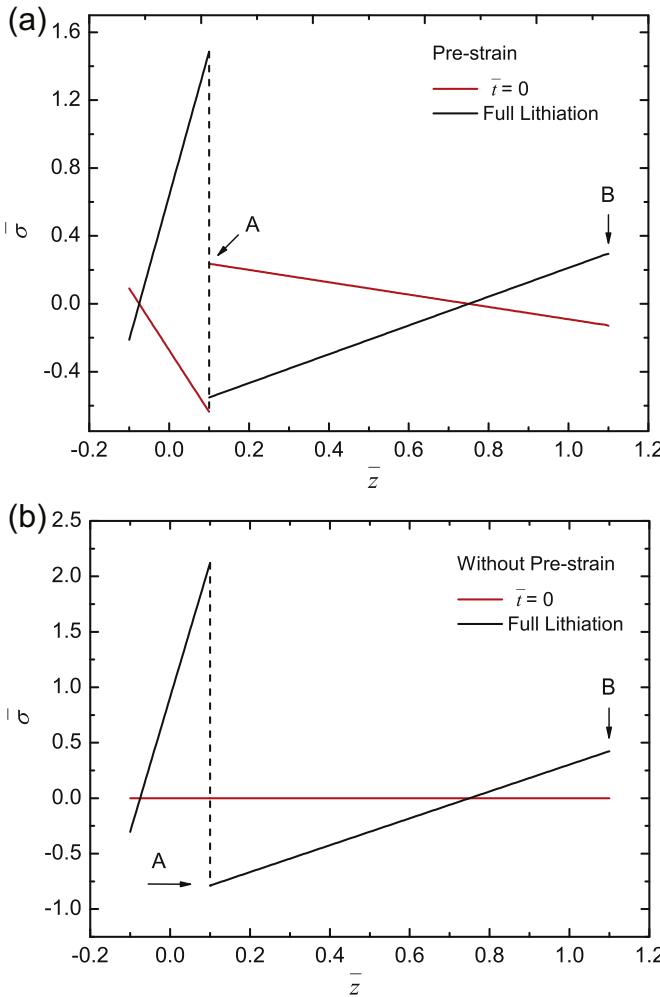
The stress drop with varying time is shown in Fig. 3. As time increases, the lithium-ion concentration of electrode film rises at the interface. Consequently, the stress drop is a monotonically increasing function of time. With respect to the case with pre-strain, the dimensionless stress drop is remarkably lower than the case without pre-strain, which is beneficial to preventing debond and delamination of the electrode–collector bilayer structure [29].

Finally, one problem should be proposed and discussed to preferably tailor built-in stresses in the following section.

Though the pre-strain effectively reduces diffusion-induced stresses, an initial stress field should be generated when the pre-strained electrode film is bonded to the current collector before lithium-ion insertion. In addition, the critical diffusion-induced stresses occur at the stage of full lithiation. Therefore, we give the results of the biaxial stress at these two stages in Fig. 4(a and b). For the case with pre-strain, the maximum tensile stress of the electrode appears at the electrode–collector interface (denoted by A) for  $\bar{t} = 0$  or at the upper surface (denoted by B) when full lithiation, and which is larger relies on the value of pre-strain. Nevertheless, there exists a competition. That is, the tensile stress increases for A and decreases for B as the pre-strain increases, or vice versa. As a result, the best condition is that making the two tensile stresses be equal by tuning the pre-strain. For the case without pre-strain in



**Fig. 3.** Stress difference of the current collector and electrode film at the interface with varying time.



**Fig. 4.** The biaxial stress of initial time and full lithium-ion insertion in two cases: (a) including pre-strain and (b) without pre-strain.

Fig. 4(b), no stress is produced at  $\bar{t} = 0$ . When the electrode is fully lithiated, diffusion-induced stresses are much larger compared with those in Fig. 4(a), especially the maximum stresses at the interface and the upper surface of the electrode film.

#### 4. Conclusion

In summary, we report a strategy of pre-strain applied to the structure of electrode film bonded to the current collector, aiming at reducing built-in stresses of electrode–collector bilayer due to lithium-ion diffusion. According, a model is developed to study the effect of pre-strain on mechanical stress of the electrode–collector structure. The results of our model show that pre-strain greatly alleviates diffusion-induced stresses of active electrode film and current collector, especially stress drop at the electrode–collector interface and the maximum tensile stress at the upper surface of electrode film. In addition, tensile stresses of two electrode film surfaces should be modestly tailored by tuning pre-strain, avoiding brittle fracture. As a result, this work can contribute to preserving structure integrity of electrodes, and further improve storage capacity and cycling stability of lithium-ion batteries. However, we state that the pre-strain approach reported here merely applies to the electrode with infinitesimal deformation, such as LiCoO<sub>2</sub>, LiMn<sub>2</sub>O<sub>4</sub>, and LiFePO<sub>4</sub>. With respect to the electrode undergoing large deformation, the pre-strain should be enlarged to achieve the desired results, which may trigger brittle fracture.

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#### Appendix

The driving force of lithium-ion transport is the gradient of chemical potential  $\mu$ . For an ideal solid solution, the chemical potential can be expressed as [30]

$$\mu = \mu_0 + RT \ln X - Q\sigma_h, \quad (\text{A.1})$$

where  $\mu_0$  is a constant,  $R$  is gas constant,  $T$  is absolute temperature, and  $X$  is the molar fraction of lithium-ion.  $\sigma_h$  is the hydrostatic stress in the electrode, which is readily derived from Eqs. (2) and (5)

$$\sigma_h = \frac{2}{3} M_f \left( \epsilon_0 - z\kappa + \epsilon^* - \frac{1}{3} Qc \right). \quad (\text{A.2})$$

The species flux can be defined as [31]

$$J = -Mc \frac{\partial \mu}{\partial z}, \quad (\text{A.3})$$

where  $M$  is the mobility of lithium-ions. By substituting Eqs. (A.1) and (A.2) into Eq. (A.3), neglecting the variation of temperature, we have

$$J = -D \left( \frac{\partial c}{\partial z} - \frac{Qc}{RT} \frac{\partial \sigma_h}{\partial z} \right) = -D \left[ (1 + \theta c) \frac{\partial c}{\partial z} + \theta c \frac{3\kappa}{Q} \right]. \quad (\text{A.4})$$

$D = MRT$  is diffusion coefficient. Using Eq. (A.2), we obtain  $\theta = 2Q^2 M_f / 9RT$ . It is a positive constant and reflects the degree of the effect of the hydrostatic stress on diffusion. Here, the current density is not only related to the concentration gradient but also the curvature itself. Interestingly, the curvature  $\kappa$  can affect lithium-ion insertion/extraction. As shown in Fig. 1,  $\kappa$  is positive at the beginning, which should enhance the lithium-ion diffusion. However,  $\kappa$  turns to a negative as lithium-ions insert, and the curvature should hinder lithium-ion diffusion. According to the conservation of species,

$$\frac{\partial c}{\partial t} + \frac{\partial J}{\partial z} = 0. \quad (\text{A.5})$$

Thus, substituting Eq. (A.4) into Eq. (A.5) yields

$$\frac{\partial c}{\partial t} - D(1 + \theta c) \frac{\partial^2 c}{\partial z^2} - D\theta \left( \frac{\partial c}{\partial z} \right)^2 - D\theta \frac{\partial c}{\partial z} \frac{3\kappa}{Q} = 0. \quad (\text{A.6})$$

Noting that it is a coupled diffusion-mechanical equation due to the presence of  $\kappa$ , as a result, this coupled nonlinear equation cannot be solved solely. Therefore, Eqs. (9) and (A.6) should be simultaneously solved.

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